Interaction of T-H Dimer Ramjet Fuel With Submarine Habitability Equipment

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INTERACTION OF T-H DIMER RAMJET FUEL WITH SUBMARINE HABITABILITY EQUIPMENT

INTRODUCTION

The Applied Science Branch of the Naval Weapons Center, China Lake, California, requested through the Naval Ship Engineering Center, Code 6151C, that the Naval Research Laboratory investigate the interaction of tetrahydromethylcyclopentadiene dimer (T-H Dimer) with submarine habitability equipment. T-H Dimer is a new fuel developed to extend the range of TALOS, a ramjet-powered surface-to-air missile. Flight tests using the T-H Dimer as a replacement for the TALOS fuel, JP-5, have confirmed range increases of up to 20% [1]. T-H Dimer is defined by Military Specification Mil-F-82522 (OS) and is commercially available.

The most important units of submarine habitability equipment to be considered with respect to fuel interaction are the ${\rm CO/H_2}$ catalytic burner and the activated carbon bed. It is thought that interaction of the fuel with other units of habitability equipment (oxygen generator, ${\rm CO_2}$ scrubber, electrostatic precipitator, and air conditioner) would be insignificant.

DESCRIPTION OF T-H DIMER

T-H Dimer $(C_{12}H_{20})$ is a colorless liquid hydrocarbon having a density of 0.93 g/cc at 16°C (60°F). It is obtained by hydrogenation and fractionation of the commercially produced compound methylcyclopentadiene dimer (MCPD). These processess change the MCPD into the completely saturated T-H Dimer, which has good stability and long-term storage characteristics, qualities which MCPD does not possess. The addition of hydrogen to MCPD lowers the density of the fuel, but this effect is offset by an increase in its available heat energy. T-H Dimer has 14% higher energy per gallon than does JP-5 [1]. It has a viscosity higher than that of Number 1 fuel oil but lower than that of Number 3 fuel oil. The boiling range of T-H Dimer is 207 to 220°C (405 to 428°F), and its flashpoint is about 74°C (165°F). Chromatograms indicate that the T-H Dimer studied in this work consists of at least five isomers.

SUBMARINE HABITABILITY EQUIPMENT AND MATERIALS

CO/H₂ Catalytic Burner

The catalytic burner used on nuclear submarines is a device through which the submarine air is continuously circulated to be exposed to hopcalite catalyst at 316°C (600°F)

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The primary purpose of the burner is to oxidize carbon monoxide (CO) and hydrogen (H_2) to carbon dioxide (CO₂) and water (H_2 O). The CO₂ and water produced by the oxidation are removed from the submarine atmosphere by other types of air purification equipment, whereas there is no suitable method for removing the original contaminants.

In addition to CO and H2, the burner oxidizes many low-molecular-weight hydrocarbons which other air purification equipment cannot remove [2]. Also, it oxidizes many organic contaminants [2] of submarine air which are at the same time removed in another way, such as through adsorption by the carbon bed. The contaminants adsorbed by the carbon are removed from the atmosphere, while those oxidized in the burner are returned to the submarine in the form of oxidation products. The most common oxidation products are water and CO2, which are produced by the combustion of hydrocarbons, the major organic contaminants in the submarine atmosphere. Water and CO₂ present no additional corrosion or toxicity problems; the air conditioner and the CO2 scrubber easily remove them from the submarine air. Some contaminants, however, are oxidized or partially oxidized by hopcalite to products which are much more deleterious than their parent compounds [3]. Examples of the latter are the halogenated hydrocarbons, which are used aboard ship as refrigerants, solvents, etc. Many of these compounds are nontoxic and noncorrosive, but as they are passed through the burner they are decomposed to produce halogen acids which are both highly toxic and highly corrosive. The maximum permissible concentration of these acids in the submarine atmosphere is very low; special filters are required for their control.

If the concentration of a deleterious oxidation product in a submarine atmosphere cannot be filtered or otherwise controlled within acceptable limits, the use of its source material aboard a submarine must be restricted. Thus, it is important to determine how a material reacts in the catalytic burner before it is put into nuclear submarines. A second reason for studying the action between hopcalite and a prospective submarine air contaminant is to determine whether the contaminant poisons or reduces the activity of the catalyst.

Hopcalite Catalyst

The hopcalite catalyst used in the catalytic burner is manufactured by Mine Safety Appliances Corporation. It is a coprecipitate of copper and manganese oxides which has been analyzed as 78.3 wt% MnO₂, 13.1 wt% CuO, and 7.9 wt% ignition loss, presumably water or chemisorbed gases. The catalyst is about 6-mesh size and has an apparent density of 1 g/cm³. The catalyst used in this work was the standard material and was purchased through Navy supply channels on the military specification MIL-C-21665 (SHIPS) of December 12, 1958, amended May 11, 1959.

Shipboard Carbon Bed

Activated carbon (charcoal) is used in the air purification systems of nuclear submarines for removing trace contaminants from the atmosphere. It is packed in approximately 5-in.-deep beds through which the ship's air is passed at a linear flow rate of 27.50 m/min (90 ft/min).

Most contaminants in the submarine atmosphere come into contact with the carbon bed; it is therefore important to understand the resulting interactions. One important consideration is that the adsorption of hydrocarbons on the carbon bed may present a fire hazard. It is known that carbon saturated with hydrocarbons is susceptible to ignition at relatively low temperatures [4], and that the carbon beds of fleet ballistic missile (FBM) submarines contain 227 to 272 kg (500 to 600 lb) of carbon capable of adsorbing 68 kg (150 lb) of hydrocarbons.

Activated Carbon

The activated carbon used on nuclear submarines has an effective adsorption area of about $1500 \text{ m}^2/\text{g}$ (7×10^6) (ft^2/lb) of carbon. It will adsorb 20 to 25% of its weight of many hydrocarbons and other organic vapors from the air. A useful characteristic of activated carbon is that it is capable of adsorbing organic molecules from a humid gas stream. In fact, organic molecules can replace water molecules on the carbon surface. The carbon used in this study was the standard submarine material and was obtained through Navy supply channels.

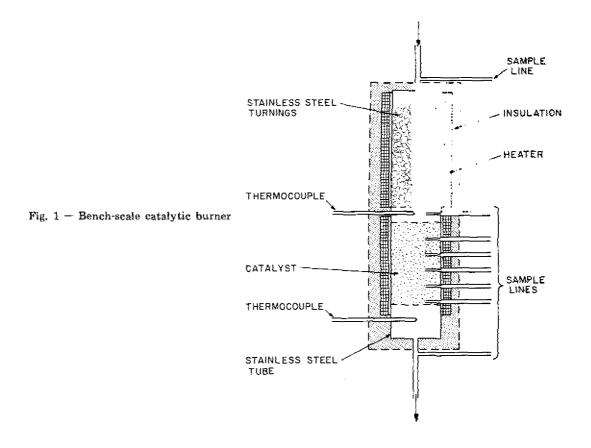
LABORATORY APPARATUS AND PROCEDURE

Bench-Scale Burner

The bench-scale burner [5] is shown in Fig. 1. It consists of a reactor with an integral preheater contained in a 71-cm (28-in.) length of 2.9-cm (1-1/8-in.) I. D. stainless steel tubing. The tubing, mounted vertically and suitably heated and insulated, is equipped with eight sampling lines of 0.3-cm (1/8-in.) O. D. stainless steel tubing to permit samples of air to be taken from the burner. These sampling tubes are located at the burner inlet, at the preheater exhaust (the space between the preheater and catalyst bed), at five points spaced at 2.5-cm (1-in.) intervals within the catalyst bed, and at the burner exhaust. The tubes are connected through stainless steel toggle valves to a gas chromatograph. Analyses of samples of burner air taken from these different sampling points reveal the reactions taking place in the burner. Space velocity, temperature, humidity, and all other operating conditions except the isze of the burner can be set to duplicate those of the shipboard burner. Thus, the reactions of a material in the CO/H2 burner can be studied in the laboratory before the material is taken aboard ship. In use, the burner was brought to operating temperature 316°C (600°F) with 0.03 m³/min (1 CFM) air passing through. With burner at 316°C. (600°F.), a portion of the 0.03 m³/min (1 CFM) air supply was diverted and bubbled through T-H Dimer, which was maintained at 100°C (212°F) in a boiling water bath. This portion of the burner air, containing T-H Dimer vapor, was then returned to the main stream and passed into the burner. Carbon monoxide was added to the burner influent by bleeding it from a pressurized cylinder through a 1-mil nozzle.

Laboratory Carbon Bed

A schematic diagram of the apparatus used to expose activated carbon to T-H Dimer vapor is shown in Fig. 2. It simulated the shipboard main carbon filter in that the carbon



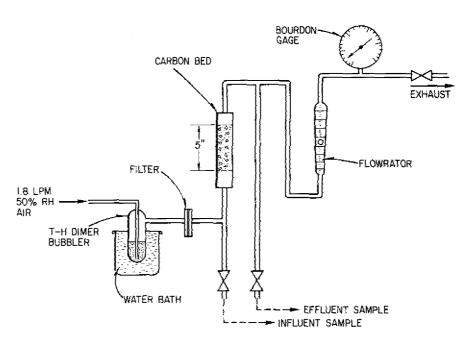


Fig. 2 — Apparatus for adsorbing T-H Dimer on activated carbon

bed was 13 cm (5 in.) deep and the linear flow rate of air through the bed was about 27.50 m/min (90 ft/min). Also, air (taken from the bench-scale burner air supply) at 50% RH was used to supply the bed. As may be seen in Fig. 2, humid air (50% RH) flowing at the rate of 1.8 pm was passed successively through a T-H Dimer bubbler, a filter, the carbon bed, a flowmeter, and an exhaust valve. The purpose of the filter was to remove aerosol and liquid droplets of T-H Dimer from the air stream and insure that the carbon was exposed only to vapors of the fuel. The exhaust valve was used to pressurize the system to 3.45 kPa (0.5 psi) to facilitate sampling the air stream. Sampling lines with toggle valves were provided on each side of the carbon bed to permit sampling of the influent and effluent air for analysis by gas chromatograph. The entire apparatus was operated at room temperature and the T-H Dimer bubbler was immersed in a water bath to minimize temperature change. All tubes and other parts of the apparatus to which the T-H Dimer was exposed before its analysis were made of stainless steel, Teflon, or glass. The apparatus was operated continuously until the carbon became saturated with T-H Dimer.

Autogenous Ignition Temperature

The apparatus used to measure the autoignition temperature of carbon saturated with T-H Dimer was the standard ASTM apparatus used to measure the autoignition temperature of liquid petroleum products [6]. Basically, the apparatus consists of a 200-m² Erlenmeyer borosilicate glass flask in an electrically heated, temperature-controlled furnace.

The standard method of measurement is to determine first the minimum autoignition temperature for 0.07 ml of the liquid petroleum product. This sample size is than increased and decreased in 0.02- to 0.03-ml increments until the minimum autoignition temperature is found. This standard method was modified to measure the autoignition temperature of the saturated carbon. With the carbon, only one size of sample was tested. This size was a weight of the saturated carbon which contained a weight of adsorbed T-H Dimer equivalent to 0.07 ml of liquid T-H Dimer. The temperature was measured with three iron-constantan thermocouples touching the flask wall at three different points and connected to a recording potentiometer. Ignition was indicated on the recorder chart by a rise in temperature and was also visually observed. When there was no ignition, a slight decrease in temperature, due to introduction of the relatively cold sample into the flask, was recorded.

ANALYSES

T-H Dimer

The T-H Dimer was analyzed with a model 810 F and M Scientific Corporation gas chromatograph using a hydrogen flame ionization detector. A 0.3-cm (1/8-in.) x 150-cm (60-in.) stainless steel column of 10% DC 200 on chromosorb G with helium carrier gas at 120° C was used. Due to the adsorption of low concentrations of T-H Dimer on the walls of containers, specially prepared standard concentrations of the fuel could not be used as standards for the analyses. Consequently, a hexane gas mixture prepared and analyzed by Scott Research Laboratories, Inc., was selected and used as a standard. The response factor of hexane relative to T-H Dimer was measured by injecting liquid samples of each

compound directly into the chromatograph. Both liquids were diluted with 50 parts of o-xylene before being analyzed. This permitted the use of liquid samples large enough to be easily measureable by syringe while keeping the hexane and T-H Dimer portions of the samples small enough to avoid overloading the column.

Several techniques for transferring T-H Dimer samples from the burner to the gas chromatograph were tested. Sample lines of both stainless steel and Teflon, heated and unheated, were tried. Samples were taken in both glass and Teflon syringes and put into the chromatograph in two different ways: passed into the sample loop, and injected directly into the instrument through a septum disc. None of these methods was entirely satisfactory because T-H Dimer was lost from the sample by adsorption on container walls. The method selected as best overall was to take the sample in a glass syringe and transfer it to a heated chromatograph gas sample loop.

Carbon Dioxide

Carbon dioxide was analyzed with a GC-2A gas chromatograph using a 0.6-cm (1/4-in.) x 180-cm (72-in.) column packed with 80/100 mesh porapak Q at 40° C. Helium carrier gas and a thermal conductivity detector at 150 mA were used. Burner air samples to be analyzed for CO_2 were bled through sample lines directly to the loop of the gas chromatograph.

Carbon Monoxide

Carbon monoxide was analyzed with a modified Total Hydrocarbon Analyzer, which is a specialized gas chromatograph [7]. In this instrument, the CO was converted to methane (CH₄) to permit its detection by the sensitive hydrogen-flame ionization detector. The sample to be analyzed was first passed through a chromatographic separation column containing equal weights of porapak Q and T to separate CO2, which would interfere with the analysis. The CO2 was removed by backflushing. The sample then was passed through a column of Type 5A molecular sieve, which separated the CO from any CH4 that might have been in the air. Both the porapak and molecular sieve columns were maintained at 65°C. From the molecular sieve column, the sample passed with a stream of hydrogen to a reactor (a bed of 10% Ni on chromasorb W at 350° C), which converted the CO to CH4. Next, the sample entered the hydrogen-flame ionization detector where the atmospheric CH_A and the catalytically formed CH4 were detected as separate peaks. A glass syringe was used to transfer samples analyzed for CO from the burner to the gas chromatograph. This method of sampling was used not because of analytical difficulties but as a matter of convenience. Peak areas for all three compounds - CO, CO $_2$, and T-H Dimer - were measured with a Hewlett Packard 3370A Electronic Integrator and Computer.

RESULTS

Bench-Scale Burner

The results of experiments in which T-H Dimer was exposed to hopcalite in the bench-scale burner are summarized in Table 1. The concentrations listed in the Table are averages

of the analyses made during four representative tests. In two of the tests, T-H Dimer was exposed to hopcalite as a single contaminant, and in two tests T-H Dimer and carbon monoxide were exposed simultaneously. Due to the adsorption of the fuel on the surfaces of the analytical and handling equipment, the concentrations of T-H Dimer listed are considered lower than the correct values. However, the ratios of inlet to exhaust concentrations or the percentages of decomposition in the burner should be more accurate than measurement of the concentrations themselves. Further, the percentage of decomposition, usually to some degree independent of the concentration, is the more useful property and the one whose measure is sought. An average of the data in Table 1 shows that about 90% of the T-H Dimer was decomposed during one pass through the burner.

Table 1
Action of Hopcalite Catalyst on T-H Dimer

Inlet Concentration (ppm)		Percent of Inlet	
T-H Dimer	СО	T-H Dimer Decomposed	
42	0	83	
21	0	88	
113	94	95	
86	69	91	
		90 Average	

It is not considered significant that higher percentages of the T-H Dimer were decomposed in the two tests in which carbon monoxide was also present as a contaminant in the burner air. The limits of error in measuring T-H Dimer concentrations are sufficient to account for variations of 83% to 95% in the measured amount of decomposition of the fuel. The conclusion is that the presence of carbon monoxide has no measurable effect on the catalytic decomposition of T-H Dimer over hopcalite catalyst.

An accurate measurement of the amount of fuel oxidized to completion, in both the preheater and the catalyst bed, can be made by analyzing the burner air for carbon dioxide (CO_2) . The gain of CO_2 is directly proportional to the amount of T-H Dimer burned. Such CO_2 analyses were made for the T-H Dimer fuel. These analyses showed that no CO_2 was produced when the T-H Dimer passed through the preheater. Therefore no fuel was decomposed in the preheater, and the entire 90% oxidation was due to catalytic action.

In addition to the action of the catalyst on the fuel, the converse action of the T-H Dimer on the catalyst must be considered. Here, the important thing to determine is

whether exposure to T-H Dimer poisons the hopcalite. Certain compounds have a poisoning effect on catalysts such that, in their presence, the catalyst has a reduced capability for oxidizing other compounds. Further, there can be a permanent effect causing the catalyst to be less active even when the poisoning compound is no longer present.

A convenient method of determining whether hopcalite has lost activity and the extent of the loss is to measure its effectiveness in oxidizing carbon monoxide (CO) [5]. Fresh hopcalite is very effective in oxidizing CO, and its activity for CO is easily measured. The results of tests of the hopcalite catalyst with CO are summarized in Table 2. These results show that the first inch (20% of bed depth) of the hopcalite bed, which had not been previously exposed to T-H Dimer, oxidized 98% of the influent CO. While the catalyst was being exposed to CO and T-H Dimer simultaneously, the first inch of catalyst bed oxidized only 69% of the influent CO. After work with T-H Dimer was completed, the hopcalite was treated for about 72 h with cool, humid, contaminant-free air. After this treatment, the hopcalite was exposed to air contaminated with about 100 ppm of CO. As may be seen in Table 2, the first inch of hopcalite bed oxidized 87% of the influent CO at this time. Thus it is seen that the activity of hopcalite for CO was reduced in the presence of T-H Dimer and that the lost activity was only partially regained. The T-H Dimer permanently damaged the catalyst.

Table 2
Action of Hopcalite Catalyst on CO

1114	let Concen- ation of CO Inlet Concentration of T-H Dimer	Percent of Influen	t CO Decomposed
Inlet Concen- tration of CO		In First Inch of Catalyst Bed	In Full Depth of Catalyst Bed‡
166	0*	98	100
70	115	69	100
107	0†	87	100

^{*}Before catalyst exposed to T-H Dimer.

The action of hopcalite in decomposing T-H Dimer and CO can be described in a more informative manner than that of Tables 1 and 2. As discussed in a previous paper [5], the conditions existing in the bench-scale reactor (and also in the shipboard reactor), including the high-temperature, turbulent gas flow and large excess of oxygen, make it reasonable to assume that the reaction in the catalyst bed is of first order. Experience with various reactants has reinforced this assumption. The following expression can be used to describe the first-order reaction:

$$-\ln C_Z = KZ, \tag{1}$$

where C_Z is the concentration of reactant, as a fraction of the input concentration, remaining at bed depth Z. Bed depth Z is expressed as a fraction of the full bed depth,

[†]After catalyst exposed to T-H Dimer.

[†]Catalyst bed is 127 mm (5 in.) deep.

and K is the effective rate constant. The rate of decomposition in the reactor may be only partly determined by the chemical activity, with heat and mass transport effects also being significant. However, under the fixed operating conditions used in this work, it appears sufficient and practical to combine these variables into the one effective activity constant denoted as K in Eq. (1).

Equation (1) is plotted in Fig. 3 in terms of 1 - C_Z (the fraction of input reactant removed by the catalyst) vs the bed depth Z for five different values of K. The three higher curves summarize the measured activities of hopcalite for CO. They represent the same data as that presented in Table 2. The curve drawn at a K value of 20 shows the activity of fresh hopcalite (not previously exposed to T-H Dimer) for CO. The curve at a K of 6 describes the activity of hopcalite for CO in the presence of T-H Dimer. The curve at a K value of 10 shows the activity of the catalyst, which has been previously exposed to T-H Dimer, for CO. Even though all CO is removed from the air in each case, the three curves clearly show that the simultaneous presence of T-H Dimer reduces the activity of hopcalite for CO. Further, a significant portion of this lost activity is not regained after exposure to T-H Dimer has been stopped and the catalyst exposed to cool, humid, contaminant-free air for a period of 72 h. The three curves illustrate both the temporary and permanent poisoning effect which the T-H Dimer has on the hopcalite.

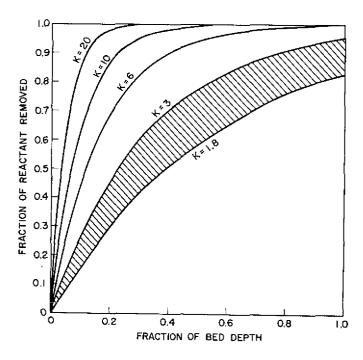


Fig. 3 — Catalytic decomposition of T-H Dimer and CO over hopealite at 600° F as a function of hopealite bed depth and for various values of the effective activity constant K

The two lower curves with the cross-hatched area between them represent the data presented in Table 1. These curves show the variation in the measured activity of hopcalite for T-H Dimer (83% to 95% removal of influent T-H Dimer during one pass through the burner). As shown in Table 1, part of these measurements were made while T-H Dimer and CO were simultaneously passed over hopcalite, and part were made while T-H Dimer was the sole contaminant. However, the variation in the data is considered to be a result of experimental error and not of the effect of CO. The data are treated in this way for three reasons: (a) it is difficult to make accurate analysis of the T-H Dimer so that the observed deviation of the results is not unexpected, (b) past experience has shown that low concentrations of CO have little if any effect on the activity of hopcalite, and (c) if CO did have an effect on the oxidation of T-H Dimer, it would be expected to be the opposite of the effect indicated by the data.

Carbon Bed

The activated carbon bed was continously exposed to T-H Dimer vapor for 9 days in the apparatus shown in Fig. 2. After that period of exposure, analyses of the influent and effluent air indicated that the carbon bed was not adsorbing T-H Dimer and, consequently, must have been saturated. The carbon adsorbed a weight of T-H Dimer equal to 30% of its own weight.

Autogenous Ignition Temperature

Samples of carbon saturated with T-H Dimer were tested in the ASTM apparatus [6] at various temperatures ranging from 538°C (1,000°F) to 238°C (460°F). Its autoignition temperature was found to be in the 249°C (480°F) to 254°C (490°F) range.

Samples of liquid T-H Dimer (0.07 ml) were found to have autoignition temperatures in the same range as the saturated carbon 249° to 254°C (480° to 490°F).

Clean activated carbon containing no adsorbed material when tested for autoignition at 538°C (1,000°F), gave no evidence of ignition which could be detected by visual observation or examination of the temperature record. However, some of the carbon granules were changed in color from black to ash gray by the heat.

DISCUSSION

It is very difficult to make accurate analyses of low concentrations of T-H Dimer because of its propensity for adsorbing on the walls of containers. This property of the fuel made it impossible to prepare a precisely known concentration of T-H Dimer (in a carrier gas) which was stable enough to be used as a standard for the analyses. Stable concentrations of gas mixtures ordinarily can be prepared by compressing the component gases, in the proper proportions, into stainless steel bottles. T-H Dimer, from a standard mixture prepared in this way, adsorbed on the inner walls of the bottle and reduced the concentration of the fuel in the gas phase by some unknown amount. This was demonstrated by

heating the bottle and analyzing samples of gas taken from the hot bottle. Higher bottle temperatures produced higher concentrations of T-H Dimer in the samples. Consequently, despite efforts to use the most suitable sampling method, the T-H Dimer analyses made in this work are doubtless in error on the low side. This is confirmed by the fact that the CO₂ analyses showed that an average of three times as much T-H Dimer was decomposed in the burner as the amount indicated by the T-H Dimer analyses. However, the fact that T-H Dimer was detected in the burner exhaust proves that some of it passed through the burner unoxidized. Further, if the analyses of the T-H Dimer in both the burner inlet and exhaust were low, their ratio or the proportion of the fuel passing through the burner unoxidized may be a good approximation. The adsorption of the T-H Dimer in the area of the hot catalytic bed should be minimal.

The behavior of the T-H Dimer should not affect any of the measurements made other than that of the proportion oxidized in the burner. The CO₂ analyses measured the quantity of T-H Dimer oxidized to completion in the burner and also proved that none of it was oxidized in the preheater. The CO analyses accurately measured the poisoning effect which the T-H Dimer had on the hopcalite. Measurement of the load of T-H Dimer which the activated carbon would accept and the spontaneous ignition temperature of the saturated carbon did not depend on the T-H Dimer analyses.

SUMMARY AND CONCLUSIONS

The action of hopcalite catalyst at 316°C (600°F) on T-H Dimer in ppm quantities has been studied using a bench-scale burner which simulates the CO/H₂ burner of nuclear submarines. Also, the action between the carbon bed of nuclear submarines and T-H Dimer was investigated. In the latter study, the capacity of the carbon for adsorbing T-H Dimer vapor and the autogenous ignition temperature of the saturated carbon were measured. The following observations and conclusions were made.

- 1. The hopcalite oxidizes approximately 90% of the inlet T-H Dimer.
- 2. The presence of T-H Dimer significantly reduced ability of hopcalite to oxidize CO, even though all the inlet CO was oxidized in the 5-in.-long (127 mm) burner. Only part of the lost activity for CO was regained after exposure to T-H Dimer was discontinued. Thus T-H Dimer has a poisoning effect on hopcalite and permanently reduces its activity.
- 3. The presence of CO does not reduce significantly the activity of hopcalite for T-H Dimer.
- 4. Activated carbon will adsorb an amount of T-H Dimer equal to 30% of its own weight.
- 5. The autogenous ignition temperature of the carbon saturated with 30 wt% T-H Dimer is the same as that of the liquid T-H Dimer. It is in the 249°-C (480°-F) to 254°-C (490°-F) temperature range.

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